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RESEARCH AND TECHNOLOGIC WORK ON EXPLOSIVES, EXPLOSIONS, AND FLAMES: FISCAL YEARS 1955 AND 1956

By Ruth F. Brinkley and Robert W. Van Dolah

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RESEARCH AND TECHNOLOGIC WORK ON EXPLOSIVES, EXPLOSIONS, AND FLAMES: FISCAL YEARS 1955 AND 1956[1]

by

Ruth F. Brinkley[2] and Robert W. Van Dolah[3]

SUMMARY AND INTRODUCTION

This report is the 17th of a series originally issued annually, and more recently bienially, to acquaint the reader with the work of the Division of Explosives Technology, Federal Bureau of Mines. It differs from preceding reports in that its material is presented in two parts: Part I reviews briefly the overall activities of the Division during fiscal years 1955 and 1956;[4] part II presents in abstract form, the publications of the Division during that period. As it is not unusual for research completed in the course of one report period to be published only in the following period, the Bureau believes that the present approach will give a more accurate presentation of its work for the period considered. The Bureau hopes too, that the somewhat more concise presentation will prove convenient to the reader.[5]

PART I - RESEARCH AND TECHNOLOGIC ACTIVITIES

The activities of the Division during fiscal years 1955 and 1956 reflected the steadily growing preoccupation with factors affecting the safety of permissible explosives and those affecting the tests used for approval of these explosives. Findings by a team of French investigators prompted a study of the influence of atmospheric moisture on the ignition of firedamp by explosives(1).[6] With 11 out of 57 field samples[7] failing to pass schedule tests for minimum safety requirements, the program for improving the safety of permissible explosives with a record of field-sample failures continued actively. Manufacturers were authorized to modify the formulations of six more brands of such permissibles by addition of sodium chloride (approximately 3 percent). Detonation velocity data of 16 permissible gelatins were revised using tetryl boosters. As part of the Division's schedule-testing services, close to 6,000 tests were run on permissibles, other types of explosives, and hazardous chemicals. Six new permissibles were tested and approved, bringing the active list of permissibles to 159, as of December 31, 1956. Two modifications of the Chemecol blasting device and two Hydrox blasting devices were approved for use in underground coal mines, bringing to 11 the number of blasting devices on the active list. The published schedule for tests on permissible explosives was revised.[8]

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[1] Work on manuscript completed April 1959.

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[4] As in other years, this review does not include activities such as security-classified research and investigations of a confidential nature, which are reported only to those immediately concerned, and short-term programs of a very limited scope, the results of which will be included in future summary publications.

[5] Additional information concerning individual unrestricted investigations is available upon request.

In the United States, total consumption of solid explosives increased somewhat in 1955 as compared with 1954 and then rose sharply in 1956.[9] The consumption of permissibles remained well below that of 1951 and 1952 (96.5 million pounds in 1956 as compared with 107 million pounds in 1951), due partly to the steadily growing use of mechanized equipment for large-scale coal-mining operations, but caused primarily by reduced coal production. The relative consumption of black powder remained low with a marked decrease in 1956.

The steadily growing use of mechanized equipment in coal mines created new safety problems, which were met by special investigations. Thus, the use of compressed air for blasting coal led to an investigation of ignition hazards associated with the underground operation of compressors(2), and a study was made of the literature pertaining to frictional ignition of gas by hot metal

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[6] Numbers in parentheses refer to papers in Part II.

[7]

	F.Y. 1955	F.Y. 1956
Number of field samples collected	36	22
Met all tolerances	21	10
Failed gallery test 1	9	2
Failed to propagate	0	0

[8] Bureau of Mines Permissibility Schedule 1G, as published in Federal Register 58, vol. 20, March 24, 1955. (Refer to predecessor Schedule 1F and its five amendments.)

[9] Industrial consumption of permissibles and other high explosives other than liquid oxygen explosives for fiscal years 1955 and 1956, in million pounds:

	In coal mining		Total	
	1955	1956	1955	1956
Permissible explosives	78.3	95.3	79.5	96.5
Other high explosives	110.6	136.1	627.7	749.5
Black powder	4.2	3.3	8.8	5.4
Total	193.1	234.7	716.0	851.4
Permissible: Black powder ratio	18.6	28.9	-	-

surfaces and particles(3). The related problems of maintaining adequate concentrations of inert dust under accelerated conditions of coal production created by mechanized mining methods also received attention(4, 5). Assistance was given the National Fire Protection Association in setting up standards for the prevention of fires and explosions by inerting.[10] Periodic large-scale demonstrations were continued at the Experimental Coal Mine, Bruceton, Pa., for the benefit of coal-mining personnel and the general public.

The Bureau's long-standing program to eliminate industrial dust explosions was continued with a study on the prevention of coal dust explosions in coal drying plants(6). Various physical factors affecting the ignition temperature of dust clouds (layer thickness, particle size, and others) were studied, as was the development of static electrical charges by dust streams. Metal screens were used experimentally for the simultaneous venting and quenching of dust explosions propagating in ducts. The explosion hazards of 155 dust samples submitted by various companies and agencies were determined in the Dust Explosions laboratory.[11]

The problem of the prevention of industrial gas explosions continued to receive attention(7). Limits of flammability, spontaneous ignition and decomposition temperatures, flame-propagation rates and stabilities were determined for approximately 40 potentially flammable gases and liquids over a wide range of temperatures (-110° to 600° C.) and pressures (0.25 to 680 atm.) likely to be encountered in practice. The effect of the surrounding atmosphere on these values was investigated using air, oxygen, chlorine, nitric oxide, nitrous oxide and nitrogen dioxide as oxidants. The program for the study of the explosibility of aircraft fuels and fluids under flight conditions, initiated for the Department of the Air Force in 1950, was continued actively. The problem of possible explosions in warning systems that make use of noxious gases (stench-warning systems) was studied(8). The Bureau of Mines apparatus for measuring spontaneous-ignition temperatures of vapor-air mixtures was modified to permit more rapid and accurate determinations(9). The campaign for safer conditions in hospital areas using anesthetic gases continued with numerous lecture-demonstrations and some laboratory research on the hazards of static electricity.[12]

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[10] National Fire Protection Association Committee, Tentative Standards for Fire and Explosion Prevention by Inerting: N.F.P.A. Pamphlet 69-TR, August 1955, 46 pp.

[11] Materials examined included: Industrial plant dusts; coal mine dusts; aluminum, zinc, iron, titanium, boron, aluminum-iron, aluminum-mica, aluminum-magnesium, nickel-aluminum, and other metal alloys; iron pyrite ores, molybdenum disulfide, phosphorous pentasulfide; cornstarch, cottonseed meal, tobacco, soybean meal, and other agricultural dusts; Irish moss, flavoring compounds, wood flour, rubber; cellulose acetate, alpha cellulose, nylon, carboxymethylcellulose, phenol formaldehyde resin, hydrocarbon polymers, and other plastics; aspirin and other drugs; coal-tar pitch; and miscellaneous chemical compounds.

[12] Guest, P. G., Lubricants on Castors in Surgery: Jour. Am. Med. Assoc., No. 157, February 19, 1955, p. 695.

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In fundamental research on explosions and detonations a new experimental approach was tried for the measurement of detonation temperatures in solid explosives(10). To obtain a better understanding of the transition from deflagration to detonation in combustion processes, a photographic study was made of such transitions in gaseous systems(11). Decomposition of nitrocellulose was studied as a key to the breakdown mechanism of propellant molecules.

A series of studies on the kinetics of oxidation reactions was completed, under the partial support of the Department of the Air Force. Originally set up to provide information to be applied in the improved design of aircraft combustors, this program placed particular emphasis on the chemical kinetics of hydrocarbon oxidation as one of the least-understood phases of fuel utilization. The resulting experimental studies included various factors governing the chain reactions involved in the oxidation of carbon monoxide(12), the oxidation of formaldehyde known to be a rate-determining intermediate in hydrocarbon oxidation(13), and the oxidation of acetaldehyde as a rate-controlling intermediate in the oxidation of propane(14). A major point of uncertainty was the role played by the formyl radical in the oxidation of hydrocarbons such as methane; this problem was attacked by experimental photolysis of formaldehyde(15, 16) which in turn suggested a laboratory study of the decomposition of formaldehyde(17). In the course of this latter investigation, an oxygen-induced exchange between hydrogen and deuterium was discovered(18). Investigation of surface oxidation reactions observed at the molecular level with the field emission microscope was continued with a study of carbon migration on the surface of a tungsten crystal(19). Some progress was made towards the development of a mathematical theory of irreversible processes(20, 21).

In the physical study of the flame itself, emphasis continued to be on the determination of burning velocities and on the problems associated with perfecting techniques for measuring these velocities.13/ Conflicts observed in published burning velocity data obtained by various methods prompted a reevaluation of the Bunsen-burner method(22). A slot burner was developed for the production of flat laminar flames, which promised to provide more accurate burning-velocity measurements. Experimental work with the spherical bomb produced data in support of a theory of the pressure dependence of burning-velocity measurements(23). Cool flames believed to play an important role in the initial stages of hot flame formation were studied by a new technique(24). A new approach to the theory of turbulent flames was proposed, based on a novel physical model of the turbulent flame(25). To test this theory, experimental techniques were developed and applied to the physical study of the flame brush; these include smoke photography and electronic probes to measure the flame thickness.

In continuing research for the gas industry on problems of burner design, with special reference to the problem of adopting domestic burners to a wide range of fuel gases, flame-stability limits were determined for several gases

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13/ Lewis, B., Remarks on the Combustion Wave, NATO, Advisory Group for Aeronautical Research and Development, "Selected Combustion Problems", (Butterworths, London), 1954, pp. 176-178.

and gas mixtures(26). A mathematical relation was established between flame-stability data measured at room temperature and corresponding data on hot burners(27). Advances were made in the study of yellow-tipped (carbon-charged) burner flames. The experimental study of combustion in dust flames continued with emphasis on the development of instrumentation and techniques.

In addition to published research, the Bureau continued services to the National Defense effort with a number of security-classified projects carried out under the direct sponsorship of the Armed Forces and in cooperation with industrial organizations engaged in defense work. As in other years, accidents involving explosions of various types and conditions presenting possible explosion hazards were investigated at the request of civil and military authorities.

In the spring of 1956, Dr. Van Dolah, chief, and Dr. Damon, assistant chief, made an extensive tour of Far Eastern explosives installations to discuss problems of explosives manufacture, distribution and utilization. Countries visited included Japan, the Philippines, Hong Kong, Korea, Formosa, Indo China and Indonesia.

Members of the Division participated actively in scientific and technical meetings, which included the Eighth International Conference of Directors of Safety in Mines Research (1954);[14/] the Fifth Symposium (International) on Combustion (1954); and the AGARD Colloquium, sponsored by NATO at Liege, Belgium (1955). Current work of the Division was presented on such occasions, and valuable contacts were established and maintained with other groups working in related fields.

[14/] Several of the papers presented at this occasion also appeared as foreign publications:

Hartmann, I., Jacobson, M., and Williams, R., Etude de laboratoire sur l'explosibilité des charbons américains: Rev. Ind. Min., vol. 35, December 1954, pp. 1306-1309.

Hartmann, I., Nagy, J., and Christofel, F. P., Taux minimum de schistification sur le mur, les parements et en couronne d'une galerie pour empêcher la propagation d'une explosion: Rev. Ind. Min. vol. 35, December 1954, pp. 1325-1329.

Hartmann, I., Nagy, J., and Rauschenberger, J. K., Enseignements d'une campagne de prélèvement de poussière dans une mine de charbon: Rev. Ind. Min. vol. 35, December 1954, pp. 1330-1338.

Grant, R. L., Mason, C. M., and Damon, G. H., Nouvelle methode de mesure du risque présenté par les explosifs vis à vis du grisou: Rev. Ind. Min. vol. 36, January 1955, pp. 316-317.

Grant, R. L., and Mason, C. M., Le mécanisme de l'inflammation du grisou par les explosifs: Rev. Ind. Min. vol. 36, January 1955, pp. 318-320.

Hanna, N. E., Tiffany, J. E., and Damon, G. H., Inflammabilité des explosifs agréés: Rev. Ind. Min. vol. 36, January 1955, pp. 321-324.

PART II - PUBLICATIONS

Explosives Research and Testing

1. Grant, R. L., Mason, C. M., and Damon, G. H., Influence of Atmospheric Moisture on Ignition of Firedamp by Explosives: Bureau of Mines Rept. of Investigations 5224, June 1956, 10 pp.

On the basis of gallery tests, Sartorius and Thouzeau[15] have reported that there is less probability of firedamp ignition by explosives when the humidity of the gallery atmosphere is high. Because this would mean that the relative safety of an explosive decreases as the moisture content of the atmosphere decreases and could be of great importance in evaluating the incendivity of permissible explosives, further confirmation was felt to be warranted.

A small gallery was designed in which cannon, explosive, and atmosphere could be controlled precisely. Initially the system was adjusted to give an ignition probability of 0.5. The gallery atmosphere, which gave 0.5 ignition probability in 10 successive shots was considered the basic, or reference, atmosphere. Tetryl was chosen as explosive because of its reproducitility.

The results showed that under the changing conditions that ordinarily prevail in testing galleries and coal mines, humidity has a small but definite effect on the ignition of firedamp by explosives. When the oxygen content of the gallery is maintained constant, the humidity of the atmosphere has no effect on ignition probability, indicating that the role of water vapor in reducing incendivity is simply to decrease the percentage of oxygen in the atmosphere. The temperature of the atmosphere within moderate limits, has no effect on incendivity, other factors being equal.

2. Hanna, N. E., Zabetakis, M. G., Van Dolah, R. W., and Damon, G. H., Potential Ignition Hazards Associated With Compressed-Air Blasting Using a Compressor Underground: Bureau of Mines Rept. of Investigations 5223, June 1956, 33 pp.

The compressed-air method for blasting coal was first developed for use in mines where onshift blasting with explosives was prohibited. The compressed-air systems currently available--Airdox and Armstrong--dislodge coal by a high-pressure discharge of air from a pressurized shell placed in the borehole. In the original systems, stationary compressors were mounted on the surface or in ventilated areas underground. To provide greater flexibility, a mobile compressor unit was developed for use at the working face. In addition to the usual hazards associated with electric cables and motors, compression of a flammable gas-air mixture, such as might enter the compressor at or near a poorly ventilated working face, or the discharge of such compressed mixtures could constitute additional explosion hazards. To investigate these latter hazards, the effect of gas concentration, rupture pressure and method of disk rupture were investigated. The following problems also were studied: Effect of firedamp on the general operation of the compressor; formation of toxic gases due to the presence of firedamp and compressor lubricants; and the effect of high pressure on the flammability characteristics of firedamp.

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[15] Sartorius, R., and Thouzeau, G., The Interdependence of Successive Results in Shots With Explosives in the Testing Gallery; The Influence of Atmospheric Moisture: Eighth International Conference of Directors of Safety in Mines Research, Dortmund-Derne, Germany, Paper 18, 1954, 27 pp.

The investigation showed that the Armstrong compressor can be used to compress natural gas-air mixtures ranging from 0 to 10 percent without any evidence of formation of carbon monoxide or significant change in the operating temperatures of the six stages. However, there is preferential absorption of the natural gas by the compressor lubricant. Tests conducted on natural gas in air at high pressures (10,000 p.s.i.) show that the strength of the ignition source is a critical factor; the lower limit of flammability was 2.3 percent natural gas by volume. Spontaneous-ignition temperature tests in air at 9,000 p.s.i. initial pressure showed a continual decrease in the ignition temperature for gas concentrations up to 14 percent, at which concentration spontaneous ignition occurred at 240° C.

Tests to determine whether explosive atmospheres can be ignited by the discharge of an Armstrong blasting device containing various natural gas-air mixtures showed no ignitions for mixtures containing up to 5 percent natural gas, but ignition was observed with an 8-percent mixture in the blasting device. Researchers believe that the delayed ignitions were caused by the metal slug formed from the sheared disk used in the blasting device. When the device was operated under more rigorous conditions constituted by confinement in a steel borehole, ignitions were virtually instantaneous. However, the use of an impact-absorbing medium in the end of a discharge head prevented ignition of explosive gas-air mixtures. Experiments in the Crawshaw-Jones apparatus confirmed these results.

Thus, operation of the Armstrong compressor and its blasting device does not appear to create an ignition hazard if the atmosphere in which the compressor is operated remains outside the flammability limits, as prescribed by the Federal Coal-Mine Safety Act and the Federal Mine Safety Code. The concentration of firedamp required to produce a flammable mixture varies with the pressure and the blasting device--5.0 percent at atmospheric pressure to approximately 2.3 percent at 10,000 p.s.i.

Experimental Coal Mine and Dust Explosions Research

3. Hartmann, I., Frictional Ignition of Gas by Mining Machines: Bureau of Mines Inf. Circ. 7727, 1955, 17 pp.

The problem of the frictional ignition of gas by mining machines is not new. In Europe it has been recognized for over a century, especially in England, where ignition by friction has been the cause of seven explosions in the past 20 years. In the United States no disasters of this type have occurred, but several recent ignitions of firedamp in American mines have been

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attributed to the impact of metal bits on hard rock during cutting and drilling of coal. Incidents of this type may increase with the development of mechanized mining. Moreover, in rapid advances into virgin coal, unexpected faults and hard mineral inclusions may be encountered, and unusually large amounts of gas may be released from the seam. At the same time, it becomes more difficult to provide adequate ventilation at the face, and new roof-support problems arise. To call attention to the hazards associated with these new conditions, a survey was made of frictional ignition of gas by mining machines, covering experience and research in Great Britain, Germany, Belgium, and the United States.

The survey showed that flammable mixtures of gas generally are ignited by frictional heating in two ways: First, a small volume of gas is heated to the ignition temperature by direct contact with a hot part of a rubbing surface; second, small heated particles, known as frictional sparks, are projected into the gas mixture. Ordinarily, flying sparks are cooled more rapidly and are therefore less incendive than sparks that are blocked by a thermal insulator, but all frictional sparks must be considered hazardous.

In industry, most frictional ignitions are caused by metal-to-metal contacts, whereas in coal mines they are due primarily to metal-rock friction. In all types of frictional heating, the ignition probability depends on the rate of energy release. Weak mixtures of methane are more readily ignited by friction than rich mixtures. Turbulence appears to promote ignition. Sliding impact and impact under small angles are more incendive than direct impact.

In contact between rock and metal, the nature of the rock is much the more important; siliceous or quartz-bearing sandstones, closely followed by iron pyrites, present the greatest hazard. The incendivity of metals appears to be related to their position in the electromotive series. In cutting and drilling, conditions that produce fine coal dust or overload the machines must be considered hazardous.

Despite extensive research,the exact mechanism of the ignition process is not well understood; however, it is well established that friction and impact between machines and minerals can produce firedamp ignitions in coal mines. Moreover, hot spots on contacting surfaces can produce ignition when there is no visible sparking. In principle, to prevent frictional ignition, gas accumulation and frictional heating or sparking must be prevented. This necessitates adequate ventilation, proper roof-control measures, the use of cooling and quenching agents, and suitable choice in the material and design of mining equipment.

4. Hartmann, I., and Westfield, J., Rock Dusting and Sampling, Including Wet-Rock Dusting at the Bureau of Mines Experimental Coal Mine: Bureau of Mines Inf. Circ. 7755, 1956, 13 pp.16/

Modern mechanized mining has brought many economic benefits and has, on the whole, enhanced safety in the coal-mining industry. It has also

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16/ Also published in Proceedings, Kentucky Mining Institute, 1955-56, pp. 54-65.

introduced new hazards. In particular, mechanized mining has greatly increased the production and dissemination of fine coal dust in mine entries; the introduction of high-speed machines has increased the probability of incendive sparks formed by frictional contact between moving metals and mineral substances in the coal or in the adjoining rock; in gassy seams rapid extraction of coal has increased the rate of gas evolution. As a result, the problem of preventing the ignition of coal dust and the development of widespread mine explosions is more pressing than ever. The ignition hazard can best be controlled by eliminating all potential igniting sources and by adequate ventilation to prevent accumulation of gas capable of triggering a coal-dust explosion. Experience has shown that coal-dust flames can be arrested, and the development of explosions prevented by properly applying generalized rock dusting.

Unlike mine gas, which normally occurs only at certain points, enough combustible coal dust may be present on any surface to produce explosive dust clouds. Thus, to be effective, rock dust must be applied uniformly and continuously on the roof and rib surfaces as well as on the floor of coal-mine entries. The rate of application must be high enough to raise the incombustible content of the mine dust to a minimum of 65 percent. Experience has shown that coal-dust explosions in mine entries can be quenched more successfully near their point of origin. As most ignition sources occur at or near active coal faces, rock dusting in active entries must be done as close to the face as possible, and at least to within 40 feet. To neutralize fresh dust, which deposits on mine surfaces in operating mines, it is necessary to apply additional rock dust from time to time. An old but valid rule is to rock dust little but often, so that rock dust mixes with coal dust to make rock dusting more effective.

Recognizing that many coal-mine operators face economic and technical difficulties in complying with the requirements for effective rock dusting, this report considers these problems both from the operators' point of view and from long experience in the Experimental Coal Mine.

One problem is to improve adherence of rock dust to the mine surfaces. Uniform distribution of rock dust over roof and ribs is important, since, during normal application with machines, more than two-thirds of the applied dust may fall to the floor. The requirement that rock dusting in mine entries be carried to within 40 feet of active coal faces makes it necessary to apply rock dust during a working shift in rapidly advancing places. As conventional rock dusting with machines raises dense dust clouds, which may become a health hazard and impair expensive mining machines, substitute methods of rock dusting and other protective measures have been sought. One procedure is the application of wet rock dust either as a premixed slurry or by mixing dry rock dust with water at the nozzle of a rock-dusting machine.

To determine whether the dust in a given area of a coal mine contains enough incombustible to prevent the propagation of a coal-dust explosion (a minimum of 65 percent), samples of mine dust are collected and analyzed. After a study made several years ago, the practice of collecting separate road and rib-roof samples at each location was replaced by collecting a complete band or a perimeter sample from the roof, the ribs, and the top (1-inch-deep) layer of the floor dust. However, in view of the many ways in which rock dust is actually applied, the Bureau of Mines now is reexamining the advisability of again collecting separate road and rib-roof samples, at least in some locations. The adherence of wetted rock dust to mine surfaces is better than that of dry rock dust, but dispersion and mixing with coal dust are less complete, making the potential hazard of the superficial layer of float dust on the rock-dusted surfaces greater than in normally rock-dusted areas. In weak explosions this float dust may be dispersed, whereas little, if any, of the rock dust beneath it would be disturbed and the explosion could propagate for a long distance. Pending further information on this subject the Bureau recommends that a close check be kept on the condition of wet-rock dusted surfaces.

5. Hartmann, I., and Nagy, J., Investigation of Dust Sampling Methods: Proceedings of the 44th Convention, Mine Inspectors' Institute of America, Pittsburgh, Pa., June 28-30, 1954, pp. 113-132.

A number of investigations relating to the effective use of rock dust and to dust-sampling procedures in coal mines are discussed.[17]

Consideration is given to the fact that the theoretical minimum number of dust samples required to give information on the adequacy of rock dust in an entire mine working is greater than can be collected by Federal inspectors using present sampling methods. Methods proposed to alleviate this situation include collecting and analyzing supplementary dust samples by specially trained mine personnel, taking spot increment samples between strip samples, and sorting underground dust samples by visual color.

6. Brown, H. R., Dalzell, C. J., Hartmann, I., Toothman, G. J. R., and Schwartz, C. H., Fire and Explosion Hazards in Thermal Coal-Drying Plants: Bureau of Mines Rept. of Investigations 5198, 1956, 20 pp.

An investigation was made to appraise fire and explosion hazards associated with different types of coal driers. Preliminary information was obtained through questionnaires and field surveys in coal-preparation plants. Full-scale tests were conducted in the plants and supplemented by laboratory analyses. Thermal driers can be classed as three types:

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[17] For experimental background of these investigations see also:
Hartmann, I., Nagy, J., and Christofel, F. P., Incombustible Required on Floor and on Rif-Roof Surfaces of Coal Mines to Prevent Propagation of Explosives: Bureau of Mines Rept. of Investigations 5053, 1954, 7 pp.
Hartmann, I., Nagy, J., and Rauschenberger, J. K., Lessons From Intensive Dust Sampling of a Coal Mine: Bureau of Mines Rept. of Investigations 5054, 1954, 12 pp.

Type 1, in which coal is transported through drying gases by gravity, suction, and other means.

Type 2, in which the coal is conveyed in a thin bed through drying gases on shaking or vibrating screens, wire-mesh conveyor belts, or perforated traveling carriers.

Type 3, in which the coal does not come in direct contact with the drying gases. No tests were made on type-3 driers, which do not present the potential hazards encountered in types 1 and 2.

Factors considered included operating temperatures, composition and especially oxygen content of the drying gases, airflow, dust loading of the air or gas currents, fineness and moisture content of the coal, and use of water sprays and auxiliary air controls.

In addition to the general hazards encountered in operations having large amounts of dust (poor housekeeping), crowded equipment, use of open flames, unsafe electrical installations, and inadequate venting, researchers found that other specific hazards may be associated with the operation of coal driers. In particular, the oxygen content of the gases in the drier may be high enough to permit ignition of coal-dust clouds. The concentration of the coal dust during the drying cycle may be within the explosive range. Driers may be operated beyond the safe rated capacity. Gas temperatures may fluctuate widely and exceed the ignition temperature of coal dust. There may be lack of automatic or interlocking control in use of coal feed or fan failure, or lack of dust collectors or scrubbers to prevent discharge of large quantities of dust into the atmosphere.

Numerous safe operating practices were recommended for thermal coal-drying plants on the basis of these findings.

Explosion, Flame, and Combustion Research

7. Zabetakis, M. G., and Jones, G. W., Prevention of Industrial Gas Explosion Disasters: Chem. Eng. Prog., 51, September 1955, pp. 411-414

Experience has shown that two of the most useful concepts for evaluating hazards of a combustible-oxidant system are its limits of flammability and its minimum spontaneous-ignition temperature. For a diluting atmosphere (e.g., air) at a particular temperature and pressure, the lower and upper limits of flammability of a combustible vapor or gas correspond to limiting mixture compositions that represent extremes between which all compositions of the mixture are to be considered flammable or explosive. The limits of flammability of a given combustible gas depend on the diluting atmosphere (oxygen, air, chlorine) and on the temperature and pressure of the resultant mixture.

Limit-of-flammability data are presented most conveniently in a three-dimensional graph, where the limits are plotted as a function of temperature and pressure for a specified diluting atmosphere. Another useful type of graph is obtained when the limits are plotted as a function of inert-gas content in a mixture of combustible, inert gas, and oxidant at a specified temperature and pressure (fig. 1).

Limits of flammability of a given mixture of combustible gases in air at a specified temperature and pressure can be determined by a mixture law, if the limits of flammability in air of each combustible in the mixture are known at the specified temperature and pressure.

Determination of the limits of flammability assumes that the mixture is ignited by some external agent (flame, hot wire, spark). However, all combustible gas-oxidant mixtures can ignite spontaneously at temperatures that permit the onset of the oxidation reaction accompanied by generation of heat, or the initiation of certain chain reactions that cause the entire mixture suddenly to burst into flame. The pressure, contact surfaces, size and geometry

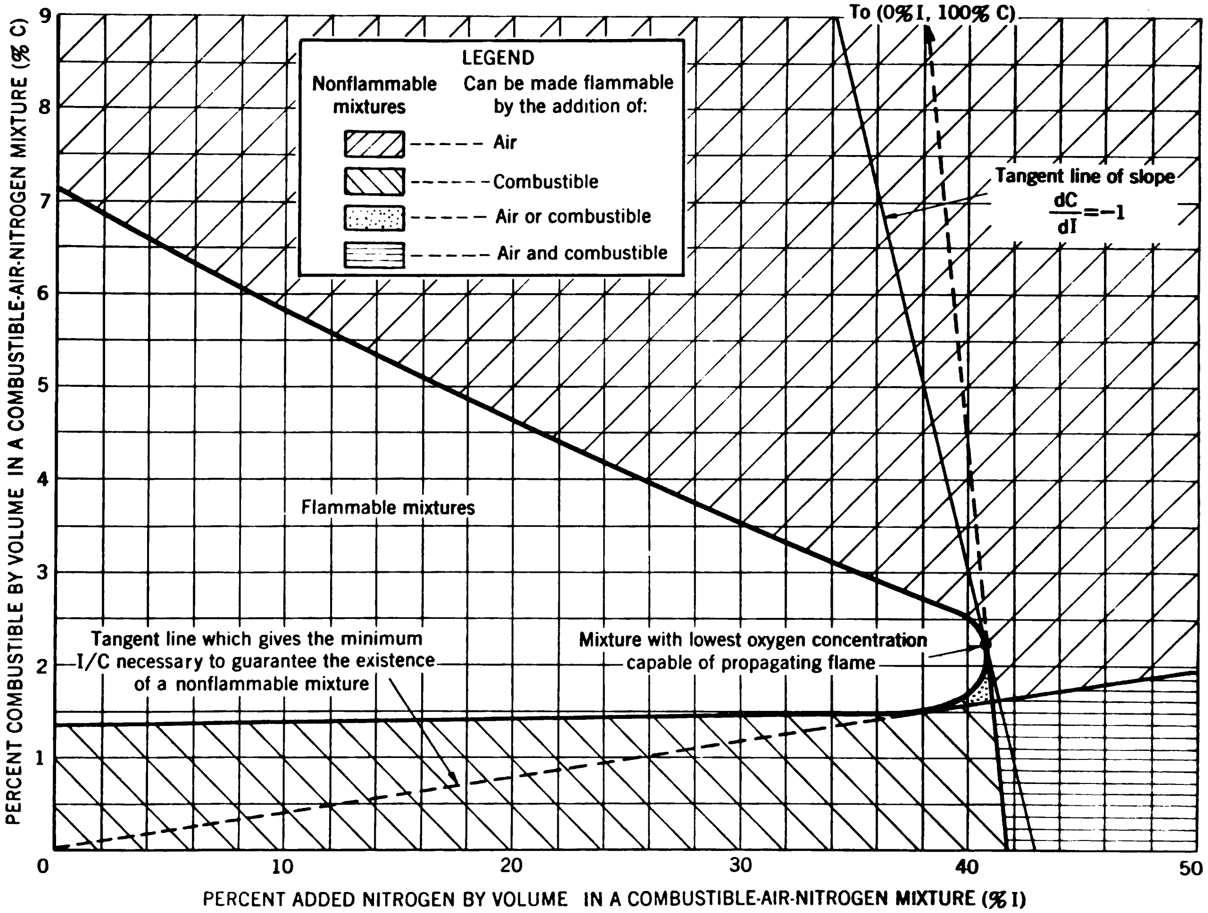

FIGURE 1. - Concentration Limits of Flammability for Aviation Gasoline Grade 100/130 Vapor-Air-Nitrogen Mixtures at Atmospheric Pressure and 80° F.

of the apparatus, the oxidant, and the combustible-to-oxidant ratio all affect the temperature at which spontaneous ignition occurs. Many systems ignite spontaneously at room temperature, but elevated temperatures are generally required. For a given set of conditions, the minimum spontaneous ignition temperatures of a family of combustibles depend on their molecular structure. In addition, the lowest oxygen concentration capable of propagating flame is nearly equal for members of a homologous family, as well as for mixtures of these members at the same temperature and pressure (fig. 2). An increase in pressure generally reduces the temperature at which spontaneous ignition may occur.

Years of research in the Gas Explosions laboratory of the Division and numerous field investigations of explosion disasters have yielded valuable information as to practical means for eliminating or minimizing gas explosions in industrial operations. These include:

1. Control of the oxygen content of the atmosphere to keep it below a critical value, operating wherever possible below the lower limit of flammability. Operations conducted above the upper limit are hazardous in that the accidental addition of air to the system may result in the formation of explosive mixtures.

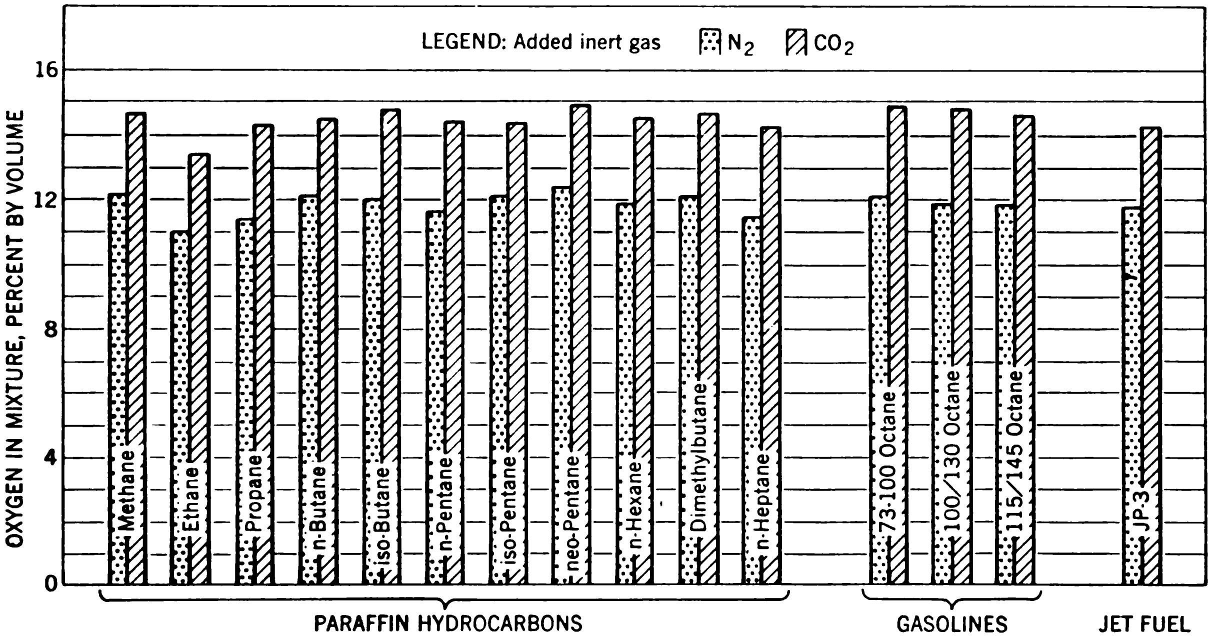

FIGURE 2. - Comparison of Minimum Quantities of Oxygen Required for Flame Propagation in Various Combustible Vapor-Air-Added Inert Gas Mixtures at Laboratory Temperature and Pressure (Constant Pressure Apparatus).

2. Whenever possible, a less-flammable material should be substituted for a particular application. Thus, halogenated hydrocarbons have become increasingly important, as the substitution of chlorine atoms for hydrogen atoms is known to make a compound less flammable.

3. Elimination of ignition sources. These include not only open flames, but sparks of static electricity, contact with hot surfaces, and other means.

4. Segregation of hazardous operations.

5. Provision of adequate ventilation.

6. Construction of smooth fireproof floors that resist penetration of liquid combustibles.

7. Provision of adequate lightweight release diaphragms that rupture readily if an explosion occurs.

8. Indicators to record the concentrations of combustibles in hazardous atmospheres.

8. Jones, G. W., Zabetakis, M. G., and Scott, G. S., Elimination of Ethyl Mercaptan Vapor-Air Explosions in Stench-Warning Systems: Bureau of Mines Rept. of Investigations 5090, 1954, 8 pp.

The Bureau of Mines has advocated the use of stenches as warning agents in metal mines and in gas-distribution systems for more than 30 years. A satisfactory stench must be relatively nontoxic, have a disagreeable and distinctive odor even in small concentrations, and be commercially available at a moderate price. In general, ethyl mercaptan (C_2H_2SH) has been considered one of the most satisfactory materials for this purpose. However, it is a highly volatile and flammable liquid compound, and may present dangerous fire and explosion hazards during use in compressed-air lines. At atmospheric pressure its limits of flammability in air are 2.80 (lower) and 18.2 (upper) percent by volume. Recent tests at the Bureau of Mines give its minimum ignition temperature in air as 280° C.

The present method of injecting stench warning agents into compressed-air lines must be considered hazardous. In many instances bottles of ethyl mercaptan are broken in high-pressure air lines, thereby producing a mercaptan-air mixture that is explosive, and may be ignited by excessively hot surfaces or other sources of ignition near the point of injection. To avoid this, ethyl mercaptan must be fed into the airstream at a controlled rate, so that the volume in the system from the point of injection to the point of passing the lower limit is very small, or it must be mixed with a suitable inert material that precludes the possibility of an explosion regardless of the rate of admission or the presence of sources of ignition. The first method is time consuming and less practical than the second.

Adding the inert gas or vapor narrows the region of flammability of combustible gases or vapors in air. Addition of sufficient inert produces a nonflammable mixture. The quantity of inert required to render a unit quantity of a combustible gas or vapor nonflammable depends principally on its specific heat. Many freons have high specific heats, and some have vapor pressures within a range that can be utilized for injection of a nonflammable ethyl mercaptan-freon mixture into a compressed-air line. The Bureau of Mines has investigated the possibility of using ethyl mercaptan mixed with freon-12 or freon-22 in proportions capable of rendering the resulting mixtures entirely flame- and explosion-proof. Freon-12 (CCl_2F_2) is a stable, nontoxic and relatively inert gas, which liquefies when compressed to 70 p.s.i.g. at 70° F. Used in conjunction with ethyl mercaptan, it discharges a mixture from a container at a pressure of approximately 70 p.s.i.g. thus providing a simple, positive method of introducing the liquid mixture into low-pressure air lines. For air-line pressures between 70 and 123 p.s.i.g., at 70° F., freon 22 ($CHClF_2$), which condenses to a liquid at 123 p.s.i.g. and 70° F. may be used. Although not as good a flame-quenching agent as freon-12 on a volume or weight basis, freon-22 does have the important advantage that its vapor pressure is 123 p.s.i.g. at 70° F., which may be the deciding factor where compressed air-line pressures are around 100 p.s.i.g.

Tests with all possible mixtures of ethyl mercaptan, air, and freon-12 show that 2.55 or more volumes of freon-12 vapor are required to render 1 volume of ethyl mercaptan vapor entirely nonflammable under all conditions of admixture with air at laboratory temperatures and pressures. Similar tests with ethyl mercaptan, freon-22, and air mixtures show that 3.80 volumes of freon-22 vapor are required for corresponding results.

As elevated temperatures and pressures widen the flammability region, a given mixture requires higher concentrations of flame-quenching agents to render it nonflammable under these conditions. Thus, when the temperature and pressure of the compressed air are increased to 200° F. and 90 p.s.i.g., respectively, the amount of added freon must be increased by approximately 10 percent.

9. Zabetakis, M. G., Furno, A. L., and Jones, G. W., Minimum Spontaneous-Ignition Temperatures of Combustibles in Air: Ind. Eng. Chem. vol. 46, 1954, pp. 2173-2178.

The standard apparatus (ASTM E-286-30)[18] used by the Bureau of Mines to determine spontaneous-ignition temperatures was modified by adding two auxiliary heaters. This eliminated temperature differentials along the axis of the flask, making measurements more rapid, accurate, and economical. The improved apparatus (I-8) measured minimum spontaneous-ignition temperatures of a number of paraffin hydrocarbons in air at atmospheric pressure. The resulting values were plotted against the average chain-length correlation parameter, L_{av}, which is a function of the number of carbons in the paraffin hydrocarbon and the length, number and position of the side groups (fig. 3). This curve can be used to predict the minimum spontaneous-ignition temperature of any paraffin hydrocarbon in air. The values fall into two general regions: The first below 290° C. (above $L_{av} \approx 5$) for compounds characterized by a long main chain and long side chains; the second, above 405° C. (below $L_{av} \approx 4$) for compounds characterized by a short main chain and side chains or a long main chain and many side chains. Another interesting curve (fig. 4) was obtained by plotting L_{av} against the critical compression ratios of various paraffin hydrocarbons. Here again the values appeared to fall into one of two regions. Activation energies for the ignition of paraffin hydrocarbons in air also were

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[18] Scott, G. S., Jones, G. W., and Scott, F. E., Determination of Ignition Temperatures of Combustible Liquids and Gases. Modification of the Drop Method Apparatus: Anal. Chem. vol. 20, 1948, p. 238.

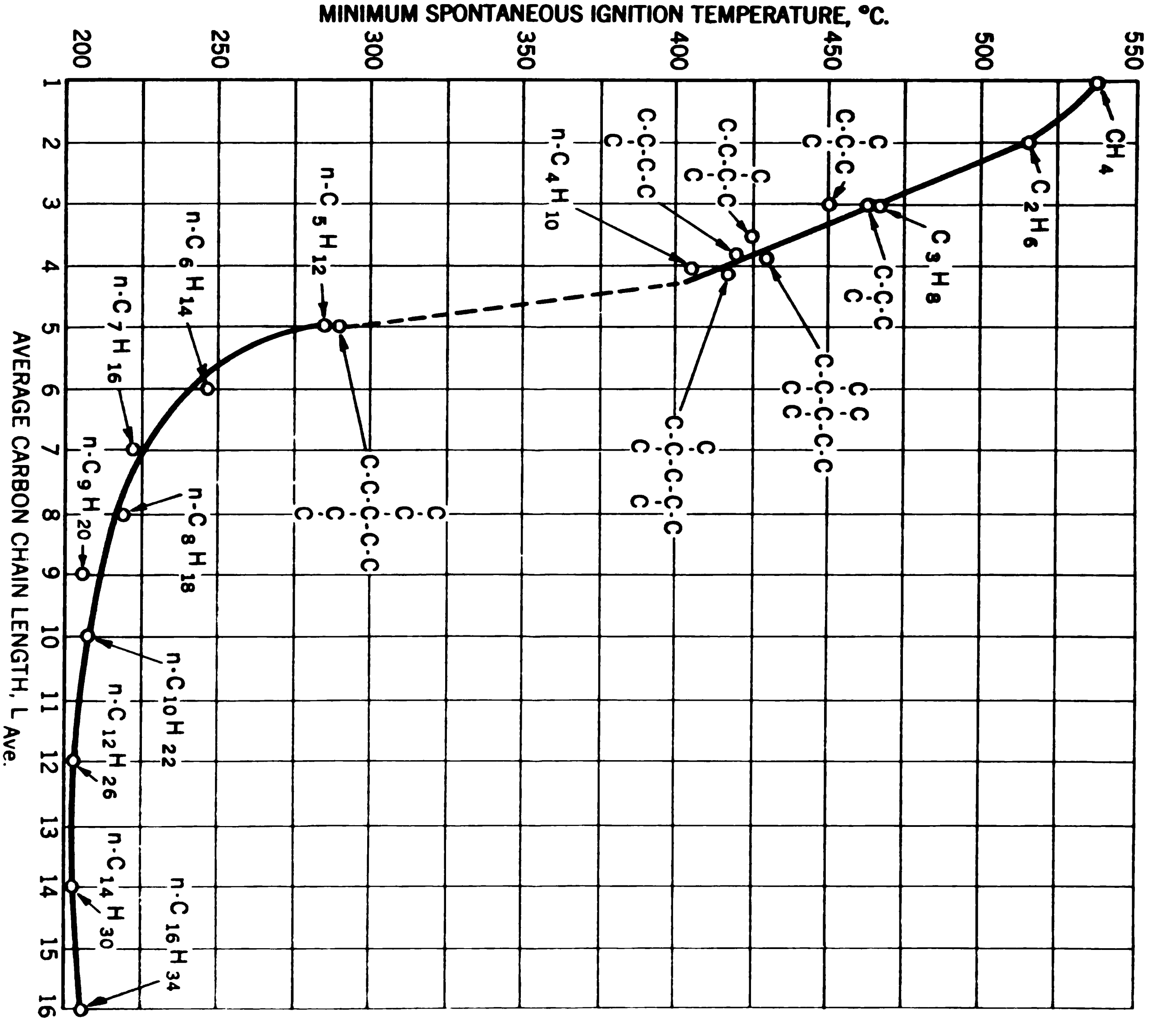

FIGURE 3. - Minimum Spontaneous Ignition Temperatures of Paraffin Hydrocarbons in Air as a Function of Average Carbon Chain Length.

calculated. Finally, the I-8 apparatus was used to determine spontaneous-ignition temperatures at reduced pressures such as occur at high altitudes. In this application, the apparatus is housed in a stainless steel shell, which can be evacuated to the desired pressure.

10. Gibson, F. C., Bowser, M., Summers, C. R., Scott, F., Cooper, J. C., and Mason, C. M., The Measurement of Detonation Temperatures: Proceedings, Second Detonation Conference, Washington, D. C., February 1955, pp. 39-49.

The temperature in the detonation front is one of the parameters most urgently needed to establish the proper equation of state for the detonation products from solid explosives. Although the measurement of this parameter has been a matter of active interest for some time, the experimental determination of definitive temperatures has not been highly successful. Earlier studies on the luminosity emitted from the exterior of charges detonated in air, water, and a partial vacuum fail to give true amplitudes. To obtain more accurate temperature data, a new method has been developed, which provides an interval of time conducive to sampling by 1-megacycle circuitry and samples the detonation radiation at the core of the charge in solid explosives. Temperatures are obtained by the two-color method based on Wien's radiation equation

$$E\lambda = c_1 \lambda^{-5} e^{-c_2/\lambda T},$$

which assumes that the radiation is black or gray body. The curve obtained by plotting the logarithm of the ratio of the radiation densities for two wavelengths, λ_1 and λ_2, against the reciprocal of the absolute temperatures is a straight line. Its slope depends on the frequencies of the band-pass filters, and its intercept is determined by the relative sensitivities of the electrical equipment that makes up each channel.

The novel physical feature of this method is the use of a transparent plastic rod embedded axially in the explosive pellet and protruding from the end of the cylinder opposite the initiated end (fig. 5). Radiation at the core of the explosive is transmitted along the plastic rod by internal reflection to the aperture of the sensing equipment. As the plastic is completely surrounded by high explosive, the explosion pressures characteristic of the detonations are maintained at the zone of measurement. The transit time

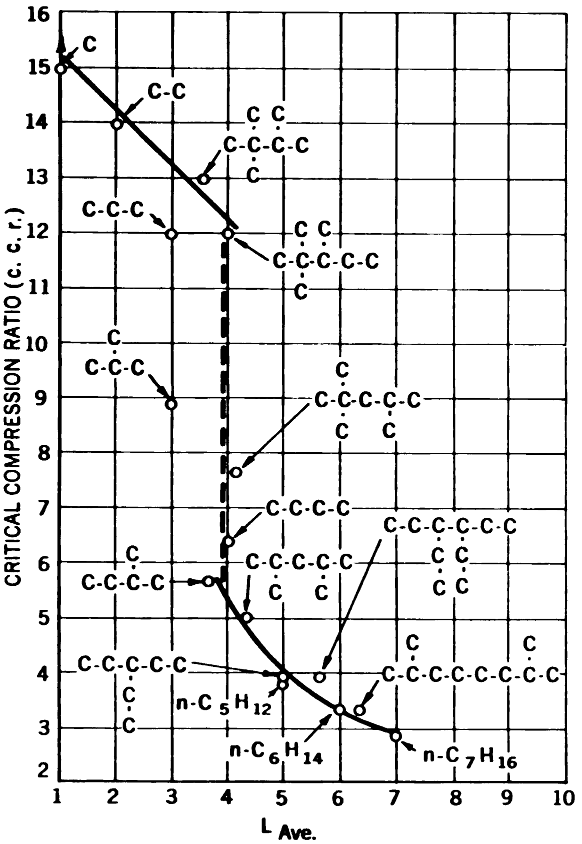

FIGURE 4. - Critical Compression Ratios of Paraffin Hydrocarbons as a Function of L_{Av}.

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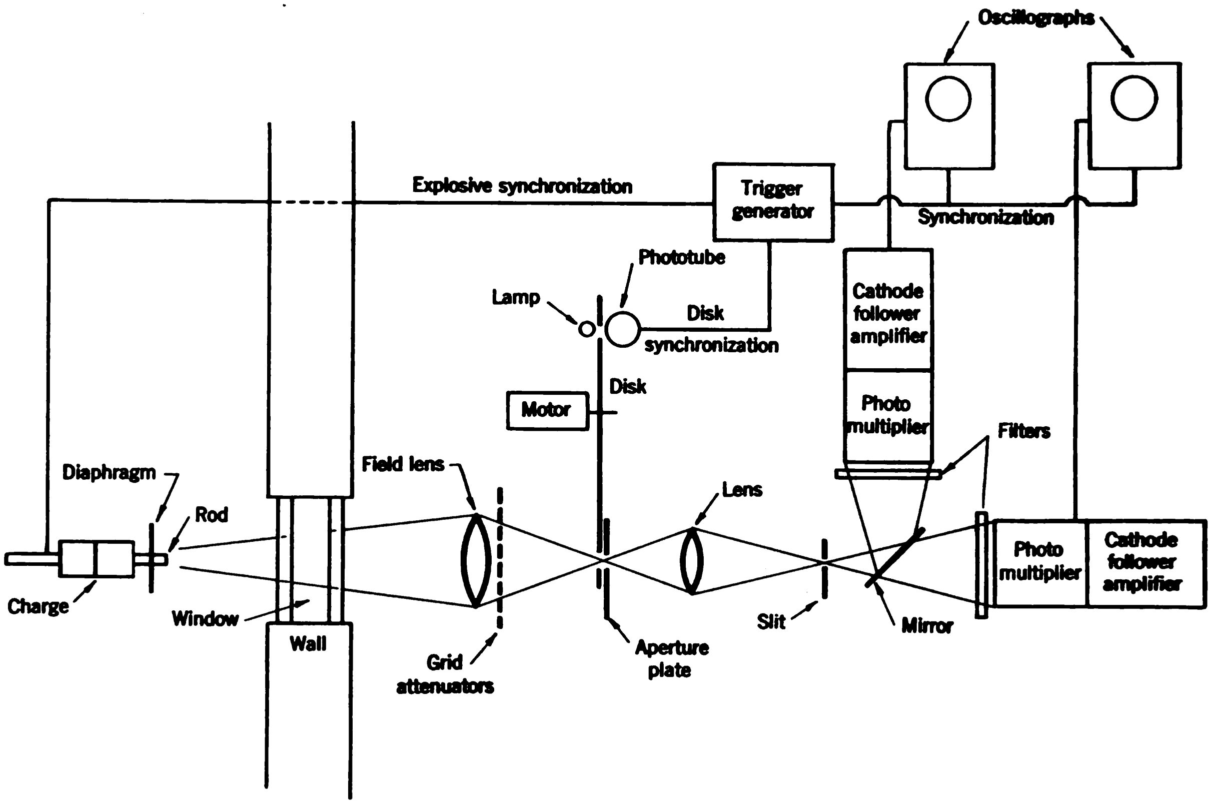

FIGURE 5. - Diagram of Apparatus for Detonation Temperature Determination.

for the detonation front is 3 microseconds or more, long enough, with respect to the response times of electronic equipment, to permit temperature evaluations after the system has attained equilibrium. Studies of explosive pellets were made with the image converter camera,[19] modified to provide streak photography. The tests were designed to establish the effect of air, propane, and the plastic rod on the radiation luminosity.

Pending complete calibration of the system, preliminary tests were made with rod pellets of tetryl and TNT in air and in propane. The order of magnitude of the resulting data is in reasonable agreement with corresponding theoretical detonation temperatures.

11. Greifer, B., Gibson, F. C., and Mason, C. M., Studies on Gaseous Detonation: Proceedings, Second Detonation Conference, Washington, D. C., February 1955, pp. 163-175.

The transition from deflagration to detonation is an important practical and theoretical problem. Information on mechanisms of detonation and deflagration was obtained from observing combustion waves in gases photographically. Careful use of precision components gave detailed and revealing pictures for

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[19] Gibson, F. C., Bowser, M. L., Ramaley, C. M., and Scott, F. H., Image Converter Camera For Studies of Explosive Phenomena: Rev. of Sci. Instr., vol. 25, February 1954, pp. 173-176.

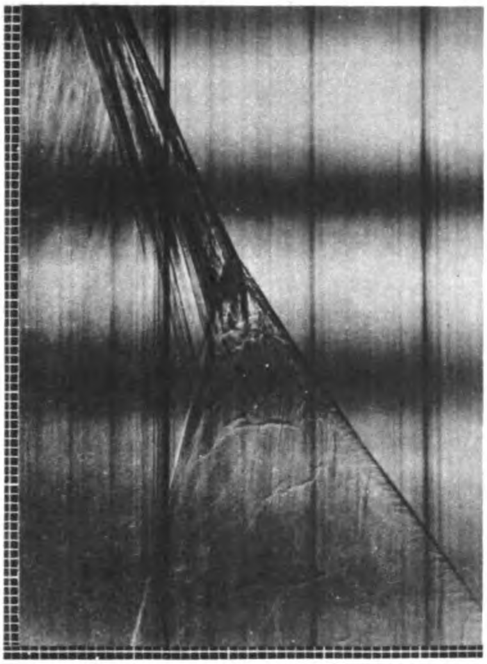

FIGURE 6. - Streak Schlieren Photograph of Transition From Deflagration to Detonation in a Mixture Containing 64.5 Percent Carbon Monoxide, 31.6 Percent Oxygen, 1.6 Percent Hydrogen, and 2.3 Percent Moisture and Inert Gases. Each horizontal scale division equals 7.06 mm., and each vertical scale division 2.82 microseconds.

various mixtures of oxygen with hydrogen and/or carbon monoxide. The explosions occurred in a steel tube of rectangular cross section with suitable observation ports and were photographed by the schlieren technique, using a rotating mirror camera. Rigid specifications for the fabrication and mounting of the parabolic mirrors gave excellent resolution. The tube was filled with a gas mixture of known composition, ignited at the open end by an electric spark. Electronic synchronization activated the schlieren light source while the combustion was within view of the camera.

For carbon monoxide-oxygen mixtures, experimental conditions were adjusted to obtain photographs of deflagration and detonation and of the actual transition from one to the other (figs. 6, 7). In certain instances, pronounced hooks or cusps appear immediately behind the shock wave and inside the reaction zone. It is possible that the peaks of these cusps represent sites of energy released in the chemical reactions that trail the shock wave. Critical analyses of the photographic data support many of the published concepts on the mechanism of detonation presented in the literature.

12. von Elbe, G., Lewis, B., and Roth, W., The Problem of the Second Explosion Limit in the Carbon Monoxide-Oxygen System: Fifth Symposium (International) on Combustion, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 610-616.

Temperature-pressure diagrams of $CO-O_2$ mixtures exhibit an explosion peninsula, which suggests that a branched-chain reaction occurs in competition with two chain-breaking reactions, one of which is predominant at low pressures and the other at high pressures. The problem was to identify the reactions responsible for these two explosion limits. Examination of existing information indicated that all three reactions were first-order with respect to the chain carrier; low pressure chain breaking (first limit) occurred at the vessel surface and the other two reactions occurred in the gas phase. To observe the gas-phase, chain-breaking reaction independently of surface chain breaking, it was necessary to make the effect of the vessel surface negligible. This was accomplished by baking out the reaction vessel and rigorously excluding water and other contaminants from the system. Under these conditions, the limit pressures were independent of the vessel diameter up to very high O_2:CO ratios.

On the basis of these experiments, a mechanism was postulated involving electronically excited CO_2 as a chain carrier and a nonbranching reaction, as follows:

$$O + O_2 + M = O_3 + M \tag{1}$$

$$O + CO + M = CO_2^* + M \tag{2}$$

where M is a third body such as N_2, O_2 or CO,

$$O_3 + CO = CO_2 + 2\ O \tag{3}$$

$$CO_2^* + O_2 = CO_2 + 2\ O \tag{4}$$

$$CO_2^* + O_2 + M = CO_2 + O_2 + M \tag{5}$$

In contrast to the hydrogen-oxygen mixture, the problem of the second limit in carbon monoxide-oxygen mixtures is very complex. Further progress will depend on careful selection of the type of experiments performed.

13. Scheer, M. D., Kinetics of the Gas-Phase Oxidation of Formaldehyde: Fifth Symposium (International) on Combustion, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 435-446.

Formaldehyde is a rate-determining intermediate in the oxidation of hydrocarbons, and the kinetics of formaldehyde oxidation have been investigated intensively. The outstanding difficulty in interpreting the literature has been to reconcile the simple kinetics reported by Axford and Norrish with the complex kinetics reported by Spence, Snowden and Style, Bone and Gardner. Lewis and von Elbe attributed this discrepancy to the destruction of intermediate peroxides by mercury vapor accidentally introduced into the Axford-Norrish system through the use of heated mercury cutoffs.

This has been confirmed by an experimental study, which showed that mercury vapor at a partial pressure of about 1 mm. Hg alters the kinetics of the oxidation reaction by destroying the intermediate peroxides. The nature and role of these peroxides also has been investigated. On the basis of this information, a mechanism is proposed that correlates existing data on formaldehyde oxidation. The essential feature of this mechanism is that performic acid is formed by a simple homogeneous, free-radical chain reaction. This performic acid is then either rapidly converted at the wall or by mercury vapor to CO, H_2O, CO_2, and H_2, or, in the absence of such decomposition, reacts with formaldehyde to yield a hydroxyperoxide, which in turn can decompose to formic acid, CO_2 and H_2. Further work is required for a complete elucidation of this mechanism.

14. Grumer, J., Early Oxidation Products of Acetaldehyde and Propane: Interpretation: Fifth Symposium (International) on Combustion, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 447-452.

Several years ago, a broad program was begun to study basic reactions associated with the nonexplosive oxidation of hydrocarbons. The initial problem was to be the mechanism of the propane-oxygen reaction, using marked C^{13} propane.[20] However, it soon became apparent that information on the oxidation mechanism of possible intermediates was an essential preliminary. To implement this study, a gasflow apparatus was designed, which provided the short contact times required to observe the early stages of gaseous reactions. Observations on propane-oxygen mixtures showed that propylene is a major early product. The yield of propylene increases with temperature and the initial O_2 concentration up to high temperatures, when oxidation may set in. Methanol, acetaldehyde, and formaldehyde also occur. Very little hydrogen is found, and the temperatures seem low for rapid oxygen-hydrogen reactions. This suggests

$$C_3H_7 + O_2 = C_3H_6 + HO_2,$$

as a possible reaction, rather than

$$C_3H_8 = C_3H_6 + H_2.$$

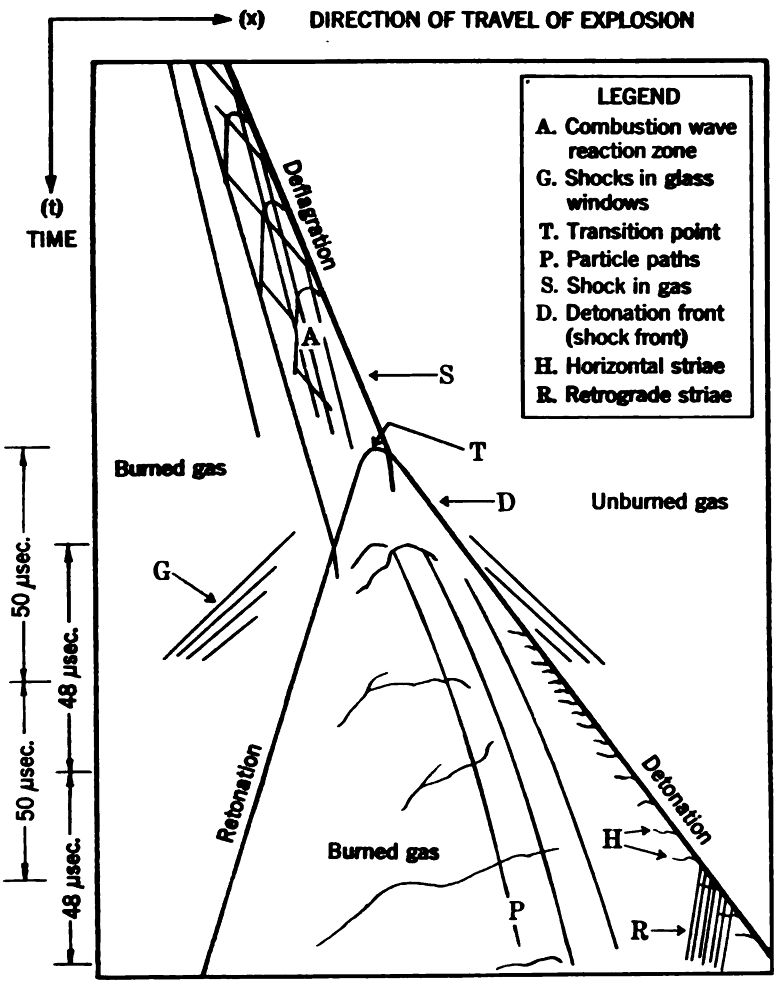

FIGURE 7. - Initiation of Detonation in a CO-O_2 Explosion.

On the basis of these findings, attention was turned to the oxidation of acetaldehyde, as a possible key reaction. Studies of early products of acetaldehyde-oxygen reactions showed that CH_3CHO is very rapidly attacked under conditions where C_3H_8 is oxidized, the attack generally beginning at the aldehydic C-H bond.

Oxidation of CH_3CHO is accompanied by rapid pyrolysis.

With both CH_3CHO and C_3H_8, methanol is the major stable oxyhydrocarbon product of oxidation. The liquid hemiacetal of CH_3OH and CH_3CHO forms as a byproduct from the gaseous reactants.

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[20] Gordon, A. S., and Heimel, S., Preparation of Propane 1-C^{13}. Electroreduction of Acetone to Propane: Jour. Am. Chem. Soc., vol. 73, 1951, p. 2942.

15. Schoen, L., Photodecomposition of Formaldehyde: Fifth Symposium (International) on Combustion, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 786-790.

In identifying the chemical species acting as chain carriers in a hydrocarbon-oxidation reaction, it is important to know if a given molecule is stable in the temperature region of the reaction. As the formyl radical (HCO) may play an important role in the oxidation of methane, the photolytic decomposition of formaldehyde was undertaken to estimate the limiting energy of dissociation of the C-H bond in this radical. Deuterium and deuterated acetylene were employed as tracers for hydrogen atoms.

The energy of the C-H bond has been reported as 27 kcal.and its activation energy for decomposition as 14 kcal./mole. The total energy requirement for complete dissociation of formaldehyde into atomic hydrogen and carbon monoxide is known (105 kcal./mole). If the energy of dissociation of formaldehyde into H and HCO can be measured, then the difference between this quantity and 105 kcal represents the molar energy of dissociation of HCO to H and CO.

The dissociation energy of formaldehyde was determined from the longest wavelength of light (3650 Å.), which brings about its photodecomposition

$$H_2CO + h\nu = H + HCO.$$

This limiting energy $\Delta H \leq 78$ kcal. was used to establish that the energy of dissociation of the formyl radical

$$HCO = H + CO$$

is equal to, or greater than, 27 kcal./mole.

16. Klein, R., and Schoen, L., Photodecomposition of Formaldehyde, Stability of HCO Radical: Jour. Chem. Phys. vol. 24, No. 5, 1956, pp. 1094-1096.

In the preceding investigation the energy of dissociation of the formyl radical (HCO) was established as being approximately 27 kcal./mole. However, the very low yields of HD hampered precise analysis of the products needed for further information on the decomposition mechanism. In the present investigation, mixtures of normal and deuterated formaldehyde were photolyzed. With this procedure, HD formation was not limited by low stationary concentrations of D, and reliable data were obtained for calculating the stability of the HCO radical.

The relative importance of the two possible processes

$$H_2CO + h\nu \longrightarrow H + HCO \quad (1)$$

and

$$H_2CO + h\nu \longrightarrow H_2 + CO \quad (2)$$

was determined by deviation of the apparent equilibrium constant for the hydrogen-isotope product species from the actual constant. A wavelength of 3650 Å. is effective for breaking the first CH bond in formaldehyde; this leads to 27 kcal. as a lower value for the heat of dissociation of HCO to H and CO (1). The intramolecular split (2) occurs not only at 3650 Å., but also at 3130 Å. Reaction (2) is considered an important, if not the major, primary photochemical reaction.

17. Klein, R., Scheer, M. D., and Schoen, L., The Pyrolysis of Formaldehyde: Jour. Am. Chem. Soc., vol. 78, 1956, pp. 50-52.

Conflicting evidence in the literature prompted an investigation to determine whether thermal decomposition of formaldehyde proceeds by a chain mechanism. It was postulated that if little or no HD occurred in the hydrogen isotope species formed by decomposition of mixtures of ordinary formaldehyde (CH_2O) and deuterated formaldehyde (CD_2O), the existence of a chain reaction could be excluded. Pyrolysis of 1:1 CH_2O-CD_2O mixtures at 547° C., followed by mass spectrometric analysis of the products, showed considerable yields of HD. H_2, HD, and D_2 are formed in proportions such that $P^2_{HD}/P_{H_2}P_{D_2}$ is a constant (3.6) over a 25-fold variation of the CH_2O/CD_2O ratio. The reaction is strongly influenced by surface pretreatment but virtually independent of the surface-to-volume ratio of the reaction vessel. Carbon monoxide and hydrogen are formed in accordance with second-order rate laws. All this gives strong support to a simple chain reaction. A competing side reaction produces methyl alcohol. Evidence indicated that this product arises from a nonchain, homogeneous process.

18. Klein, R., Scheer, M. D., and Schoen, L., The Oxygen-Induced Hydrogen-Deuterium Exchange: Jour. Am. Chem. Soc., vol. 78, 1956, pp. 47-49.

Among the final products of thermal decomposition of CH_2O-CD_2O mixtures are hydrogen and deuterium, which undergo an exchange that normally is very slow. However, in the presence of 2 to 3 parts of oxygen per thousand this exchange is greatly accelerated (100 times or more around 500° C.). It is demonstrated that small amounts of oxygen induce a chain reaction, which is initiated at the wall of the reaction vessel and terminated in the gas phase. The initiation process is probably

$$A_2 + O_2 \xrightarrow{\text{wall}} 2\ OA, \qquad (1)$$

where A represents either H or D, followed by

$$OA + A_2 \longrightarrow A_2O + A. \qquad (2)$$

The resulting chain is terminated by

$$A + O_2 + M \longrightarrow AO_2 + M, \qquad (3)$$

where M is a third body such as H_2, D_2, HD, O_2, H_2O, with AO_2 diffusing to the wall, where it is destroyed.

It was possible to calculate the total (H + D) atom concentration, a lower limit for the chain length and the rate constant for reaction 3.

19. Klein, R., The Surface Migration of Carbon on Tungsten: Jour. Chem. Phys., vol. 22, 1954, pp. 1406-1413.

An earlier study[21/] of the oxygen-carbon surface reaction on a tungsten surface with the field-emission microscope indicated the need for a study of the migration of both carbon and oxygen on the tungsten lattice. The surface migration of carbon on tungsten has now been observed with the field-emission microscope, modified by addition of a side tube containing a tantalum filament, which provides a tantalum film on the walls of the tube.

The carbon source was a carefully outgassed 5-mil-diameter graphite filament. The vacuum attained in the system, exclusive of helium, was about 10^{-12} mm. Hg. The tungsten point was shadowed with carbon and heated to a given temperature; the emission patterns were observed at room temperature after various time intervals. Migration occurs at a measurable rate about 850° K. (fig. 8). It is characterized by a sharp boundary of a form, which clearly shows that the (011) and (121) planes are avoided. This sharp boundary is attributed to strong lateral carbon-carbon interaction, with possible surface carbide formation.

An activation energy of 55 ± 7 kcal./mole was calculated for the process by applying the theory of diffusion with a sharp moving boundary.

20. MacDonald, W. N., III, and Richardson, J. M., Approximate Variational Principle in Quantum Statistics: Phys. Rev. vol. 96, No. 1, October 1, 1954, pp. 18-21.

The problem was formulation of a general approximate variational method in the quantum statistics of fermions and bosons, using the grand canonical ensemble of Gibbs and the procedures of second quantization. In quantum statistics, the Gibbs grand canonical ensemble is introduced through the density matrix of von Newmann, which can be used to formulate an exact variational principle embodying the principle of maximization of entropy. With the formalism of second quantization, this variational principle can be written, for fermions or bosons and then an approximate variational procedure can be derived from it that yields the particle states of a system of interacting bosons or fermions as well as the distribution of particles in these states. These equations yield the generalization of the Hartree-Fock equations for nonzero temperature and the corresponding extension to bosons.

21. Richardson, J. M., Variational Theory of the Radial Distribution Function: Jour. Chem. Phys., vol. 23, No. 12, 1955, pp. 2304-2308.

A theory of the radial distribution function (r.d.f.) was sought that would be simpler in structure than the existing theories and that would yield

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[21/] Klein, R., Investigation of the Surface Reaction of Oxygen With Carbon on Tungsten With the Field-Emission Microscope: Jour. Chem. Phys., vol. 21, 1953, pp. 1177-1180.

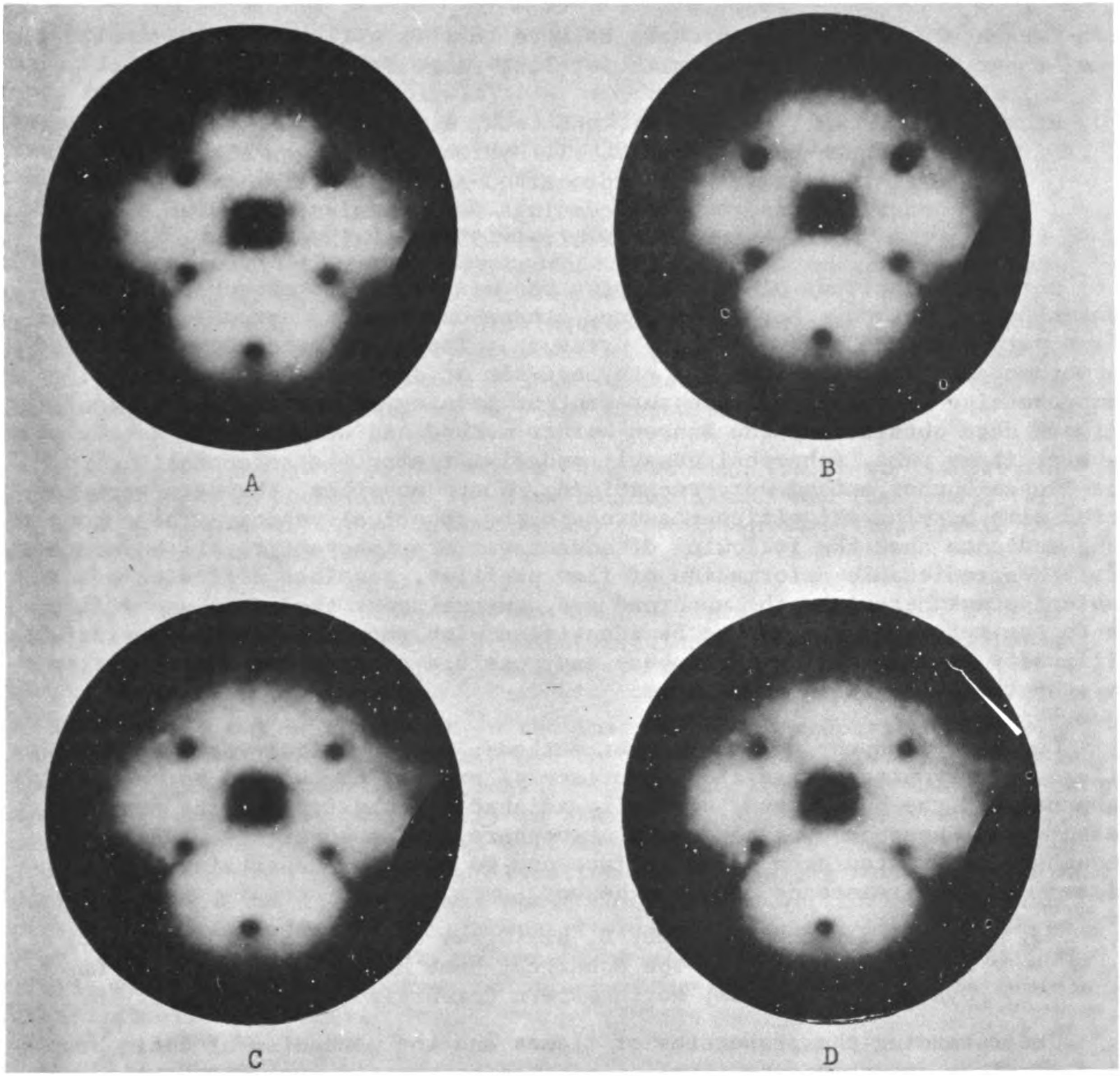

FIGURE 8. - Carbon Migration at 850° K.: A, 15 Seconds, B, 3½ Minutes, C, 55 Minutes, D, 85 Minutes.

thermodynamic functions in a more direct way. For this purpose, a variational approach to the calculation of the r.d.f. has been presented. The approximations consist in the neglect of fourth-order correlation in the entropy and use of a constant third-order correlation chosen to satisfy the third-order normalization condition. The average interaction energy, containing only pair terms, does not involve correlations higher than second order. Finally, approximate expression for the excess Helmholtz free energy is obtained as a function of the r.d.f. and macroscopic parameters. This free energy, when minimized with respect to the r.d.f. at constant temperature and density, yields an integral equation for the r.d.f. Although the theory has not yet been adequately tested, researchers believe that it will give good results for short-range forces but poor results for long-range forces.

22. Singer, J. M., Grumer, J., and Cook, E. B., Burning Velocities by the Bunsen-Burner Method. I. Hydrocarbon-Oxygen Mixtures at One Atmosphere. II. Hydrocarbon-Air Mixtures at Subatmospheric Pressures: Proceedings Gas Dynamics Symposium, Northwestern University, 1956, pp. 139-150.

Burning velocities of fast-burning gas mixtures were measured by the Bunsen-burner method. Methane-oxygen, ethane-oxygen, and propane-oxygen mixtures were measured at atmospheric pressure. The same technique was applied to methane-air, propane-air, and ethylene-air at subatmospheric pressure. As comprehensive studies on the measurement of burning velocities showed conflict between data obtained by the Bunsen-burner method and methods such as the soap bubble, flame tube, spherical vessel, and flat flame, the potentialities of the Bunsen-burner method were reexamined. Where possible, the data were compared with burning velocities measured in the spherical vessel. These comparisons indicate that the following disadvantages are inherent to all burner methods: Nonpredictable deformation of flow profiles, possible diffusion of the ambient atmosphere into the unburned gas, quenching by the port, uncertainty as to the reference outline to be identified with the combustion-wave surface, difficulty in tracking stream tubes, and possible cooling of the combustion wave by the surrounding atmosphere.

Compared with the various burner methods, the spherical-vessel method offers the advantages of a closed surface of primary combustion between the unburned and the burned gas, virtually adiabatic combustion in the zone of measurement, absence of a secondary atmosphere, and a spherical wave long enough to be treated as a plane surface and to minimize uncertainties associated with the reference outline chosen.

23. Manton, J., and Milliken, B. B., Study of Pressure Dependence of Burning Velocity by the Spherical-Bomb Method: Proceedings Gas Dynamics Symposium, Northwestern University, 1956, pp. 151-157.

Understanding the properties of flames and the mechanism of their propagation requires accurate determination of standard burning velocity. Although the burning velocities measured for the more usual gas mixtures are now generally accepted, considerable controversy exists regarding pressure dependence; results reported by different workers in this field are often contradictory. An explanation of these differences has been proposed, based on data obtained by the spherical-vessel method.

The theory underlying the spherical-vessel method has been described in detail elsewhere.22/ The diameter of the flame is photographed by a rotating

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22/ Manton, J., von Elbe, G., and Lewis, B., Burning Velocity Measurements in a Spherical Vessel With Central Ignition: Fourth Symposium (International) on Combustion, Williams & Wilkins Co., Baltimore, Md., 1953, pp. 358-363.

Lewis, B., and von Elbe, G., Combustion, Flames and Explosions of Gases: Acad. Press, New York, N. Y., 1951, p. 451.

drum camera with a schlieren optical system. The pressure record of the explosion is obtained simultaneously with the flame record. The constant-volume method of measuring burning velocity has many advantages. In particular, it eliminates secondary air and wall effects; flame-curvature effects are minimized by using large-diameter vessels and flames yielding an essentially adiabatic plane combustion wave.

Analysis of burning-velocity measurements at pressures ranging from 1.5 to 0.04 atm. shows that pressure dependence is variable and appears to be a function of burning velocity. At burning velocities below 50 cm./sec. the burning velocity varies inversely with pressure. Between 50 and 100 cm./sec. the burning velocity is virtually constant with pressure and from 100 cm./sec. upwards it increases with pressure. This suggests that all burning velocities must approach a constant value at very low pressures.

Diffusional and thermal mechanisms both are significant in flames; the first is relatively predominant for slow-burning flames and the second for fast flames. Detonability of a mixture may be correlated with pressure dependence of the burning velocity.

24. Foresti, R. J., Stabilization and Temperature Measurement of Flat Cool Flames: Fifth Symposium (International) on Combustion, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 582-589.

Cool flames may be important in the initiation and propagation of hot flames. Moreover, cool flames are known to occur in the cylinders of internal-combustion engines and may be responsible for engine knock. In the past, cool flames have been studied principally in static systems, and measurements and observation tend to be difficult as well as inaccurate, owing to wall effect. In the present investigation, a modification of the Powling burner system was used to produce a stable cool flame above the rim of a vertical burner tube. Experiments were carried out at atmospheric pressure with rich mixtures of diethyl ether-air, n-hexane-air and n-heptane-air. By adjusting the fuel-air ratio it was possible to produce cool flames, two-stage flames, white luminous flames and cellular flames.

Temperature surveys of cool flames in the ether-air mixtures, using a platinum-platinum rhodium thermocouple showed that the temperature immediately following the cool flames was 520°±10° C. (fig. 9). The rate of temperature rise preceding the cool flame was greater than predicted by heat conduction upstream from the flame. As the reaction mixture became leaner the secondary flame moved closer to the cooler flame, and its temperature rose from 800° to 1,000° C., where the two flames coalesced with white emission of carbon particles (fig. 10). With an even leaner mixture, luminous emission disappeared, and the flame became cellular and had a sharp rise both in temperature and burning velocity.

To produce cool flames in the n-heptane and n-hexane mixtures, it was necessary to preheat them. The flame-temperature profiles were very similar to those for ether-air flames, but the temperature gradient was greater. The

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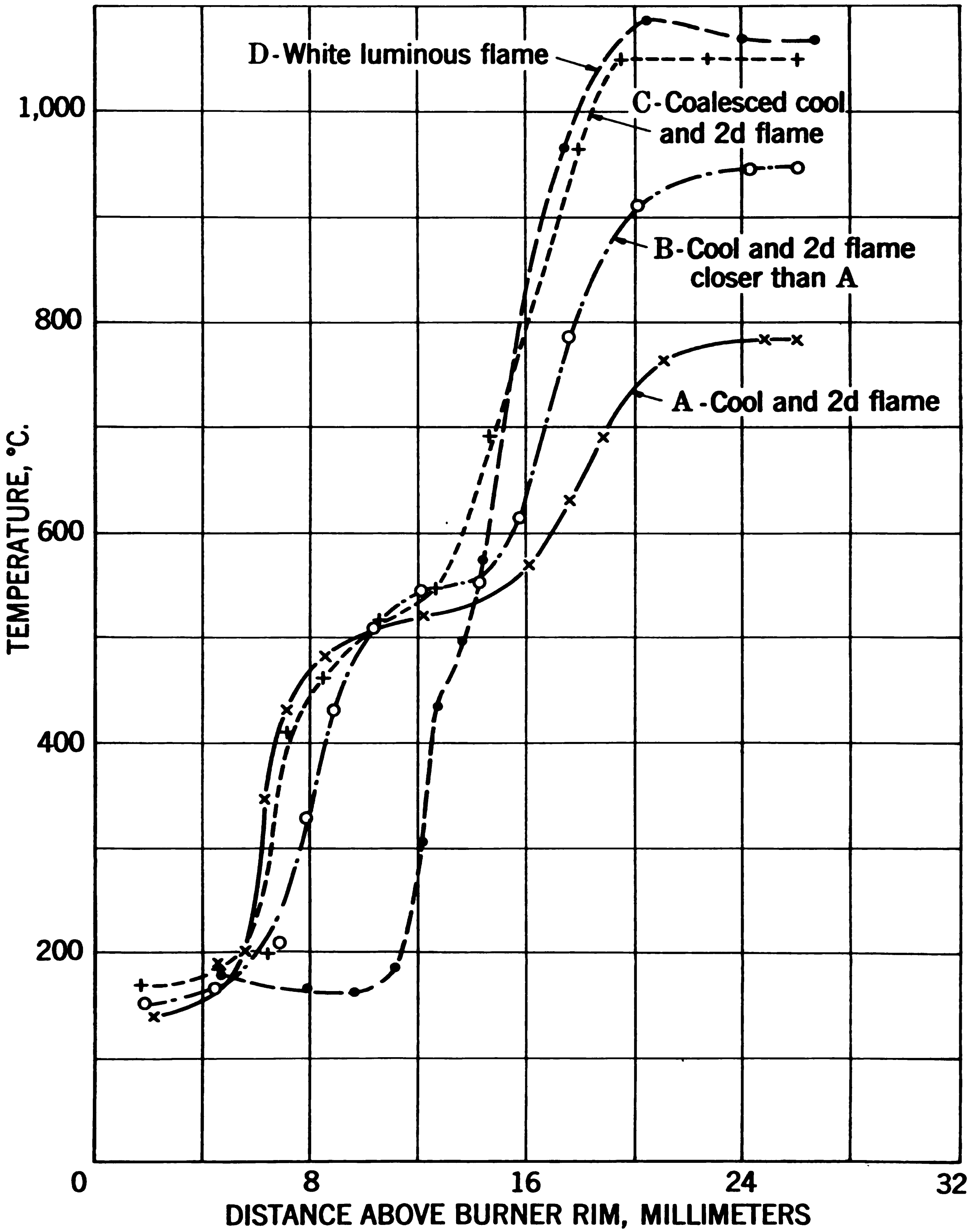

FIGURE 9. - Flame Temperature Distribution at Various Ether-Air Ratios.

temperature following the cool flame remained close to 520° C. Chemically, cool flames of hydrocarbons in air appear very similar to cool diethyl ether-air flames. In both cases the reaction rate decreases rapidly after 520° C.

25. Karlovitz, B., A Turbulent Flame Theory Derived From Experiments: "Selected Combustion Problems": NATO, Advisory Group for Aeronautical Research and Development, Butterworths, London, 1954, pp. 248-252.

A model has been proposed for the structure of turbulent flames burning in explosive mixtures, and a theory of turbulent burning velocity has been developed, based on this flame structure. The cardinal point of this theory is the calculation of the time interval during which a small portion of the instantaneous combustion wave has statistical correlation with the random motion of a certain mass of gas. Comparison of measured values of the turbulent burning velocity with the predictions of this theory points to the possibility of generation of turbulence by the turbulent flame. A mechanism has been proposed by which the turbulent flame can generate additional turbulence. A theory of this process has been developed and used to calculate the intensity of flame-generated turbulence.

The turbulence intensities calculated from measured turbulent burning-velocity data are in good agreement with turbulence intensities calculated from this theory. An independent experimental test of both theories would require direct measurement of the turbulence intensity in the flame; this is believed feasible. A relationship has been derived between the burning velocity, scale of turbulence, and the thickness of the turbulent flame brush. On the basis of this relation, measurement of the flame brush thickness by an electronic probe can yield information about the scale of turbulence in the flame. Further experimental work is required to complete the experimental test of the theory of turbulent flames and to establish its range of validity.

26. Grumer, J., Harris, M. E., and Schultz, H., Flame-Stability Limits of Ethylene, Propane, Methane, Hydrogen, and Nitrogen Mixtures: Ind. Eng. Chem., vol. 47, No. 9, 1955, pp. 1760-1767.

In studying the combustion characteristics of fuel gases used by gas utilities, the first gases considered were methane, hydrogen, and carbon monoxide and mixtures of the coke-oven type. More recently this work was extended to provide flashback and blowoff data for ethylene, propane, and hydrogen; the binary mixtures of each with nitrogen; and multicomponent fuels of these gases, particularly of the oil-gas type.

Flashback and blowoff limits of a fuel burning in free air may each be represented by a single curve of critical boundary velocity gradients versus fuel-air composition in the burner, expressed as the fuel-gas concentration fraction of stoichiometric. The two curves comprise the flame-stability diagram of the fuel. This diagram is characteristic of the fuel gas and within the wide applicability of the theory does not depend on any test

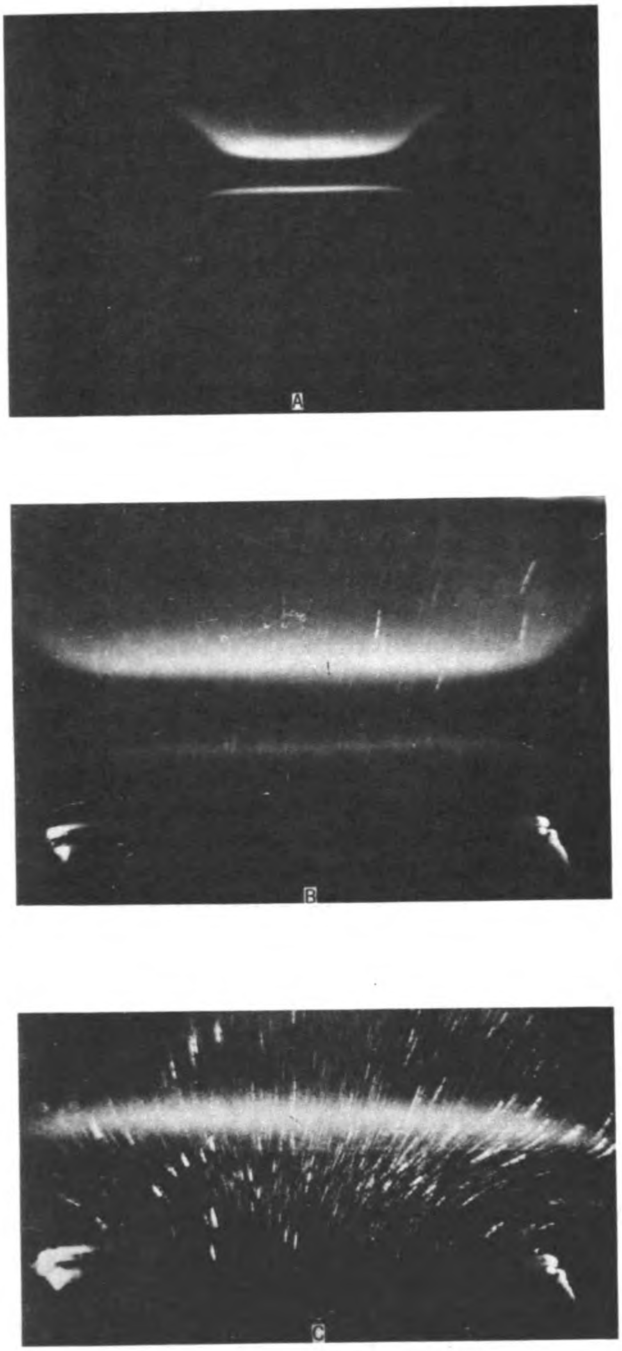

FIGURE 10. - Cool and Secondary Flames in Rich Ether-Air Mixtures. A. Two Distinct Stages of Cool and Secondary Flames. B. Two Distinct Stages Showing Particle Track Pattern. C. Coalesced Cool and Secondary Flames Showing Particle Track Patterns.

burner or any group of burners. Although such diagrams can be obtained for any gas or combination of gases by measurement in the laboratory, this would be extremely time consuming, and simple means of representing all possible combinations of fuels are needed.

The simplest method of representing binary mixtures assumes that the flame-stability limits correspond to weighted averages of the single components of the mixture; however, not all binary mixtures can be treated in this way, and a graphic method has been developed for such cases.23/

The simplest concept of the addition of nitrogen to a binary mixture is to consider it as a diluent, and this procedure has proved very successful, probably because of the high nitrogen content of all air flames. Flashback and blowoff gradients of multicomponent fuels have been approximated by systematic calculations, based on measurements of gradients of mono- and di-component fuels. In this way, flashback and blowoff data have been obtained for ethylene, propane, and hydrogen. Binary mixtures of each with nitrogen and multicomponent fuels of these gases, particularly of oil-gas type are all of interest to the gas industry.

23/ Grumer, J., and Harris, M. E., Flame-Stability Limits of Methane, Hydrogen, and Carbon Monoxide Mixtures: Ind. Eng. Chem., vol. 44, 1952, p. 1547.

27. Grumer, J., and Harris, M. E., Temperature Dependence of
Stability Limits of Burner Flames: Ind. Eng.
Chem. vol. 46, 1954, pp. 2424-2430

Intensive research on the characteristics of fuel gases and the stabilization of flames on gas burners has led to fundamental concepts of burner performance that consider the stability limits of flames in terms of the critical boundary velocity gradient for flashback and blowoff. In support of this theory, a large number of such gradients have been determined for single-component and multi-component fuels[24 25] on burners at room temperature. However, as most burners operate hot, it is of considerable practical interest to know how these room-temperature values relate to burners having hot ports. The theoretical condition for flame stabilization is that the boundary velocity gradient of the burner stream equals the quotient of the burning velocity and the quenching distance. When the appropriate gradient is known for one temperature, that gradient can be related to values at other temperatures by the temperature dependence of the burning velocity and the quenching distance. This relation has been expressed mathematically as the initial temperature of the unburned gas, the thermodynamic flame temperature, and the lowest temperature in the primary combustion zone. Although the behavior of flames is far more complex than is implied by this treatment of the effect of preheat on flame-stability limits, data obtained for methane-air and propane-air flames in the region from 300° to 600° K. show that the dimensional analyses are adequate and that the theory is generally applicable.

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[24] Work cited in footnote 23.

[25] Grumer, J., Harris, M. E., and Schultz, H., Predicting Interchangeability of Fuel Gases; Interchangeability of Oil Gases or Propane-Air Fuels With Natural Gases: Ind. Eng. Chem., vol. 44, 1952, pp. 1554-1559.

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